

## Kinetics of reactions of Cl atoms with C4 – C5 hydrocarbons over a temperature range of ~220 – 320 K

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Chlorine has been traditionally associated with marine boundary layer chemistry, however recent observations of high [ClNO<sub>2</sub>] in inland urban areas in the USA <sup>(1)</sup>, as well as significant [Cl] in volcanic plumes in Iceland, have had an impact on the importance of chlorine chemistry outside the marine environment.

Several room temperature relative-rate ratios have been reported for *n*-butane and iso-butane, differing by 20% between different authors, with some studies performed over high temperature ranges but only one reported over low temperatures. Very few previous studies have focused on Cl reactions with *n*-pentane and iso-pentane at 298 K and to our knowledge no previous temperature dependent studies have been reported for these alkanes. Reactions of Cl atoms with a set of non-methane hydrocarbons (NMHCs): *n*-butane, iso-butane, *n*-pentane and iso-pentane were studied experimentally using the Highly Instrumented Reactor for Atmospheric Chemistry (HIRAC) <sup>(2)</sup>.

Relative-rate experiments were carried out over a temperature range of 220 – 320 K at 760 Torr. FTIR and GC were used to measure rate coefficients for the Cl + NMHC reactions using an ethane reference. Relative-rate ratios obtained at 298K for all NMHCs investigated are in good agreement with recent literature data. Low temperature relative-rate ratios obtained using both GC and FTIR were in excellent agreement with each other in contrast to some previous studies. Site-specific rate data will be determined for these NMHCs and product branching fractions using deuterated compounds are planned for Cl atom reactions with other NMHCs to obtain an insight into product ratios and mechanistic information of these reactions.

### References

(1) Thornton, J. A. et al., Nature, 464, pp.271-274, 2010.

(2) Glowacki, D. R. et al., Atmos. Chem. Phys., 7, pp.5371-5390, 2007.

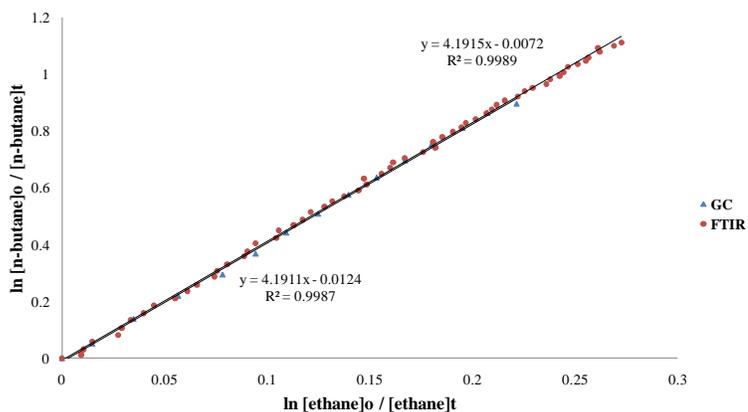


Fig.1.: Comparison of GC and FTIR relative-rate plots for Cl + *n*-butane using ethane reference at 298 K determined by GC (4.1911, ▲) and FTIR (4.1915, ●).

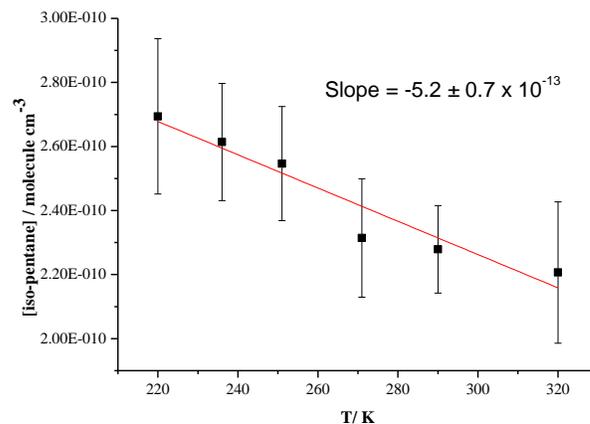


Fig.2.: Rate coefficient for Cl + iso-pentane against temperature.